1,8-Naphthyridine Complexes of Dimethylgold Halides and Pseudohalides. A Simple Case of Fluxional Behavior[1]

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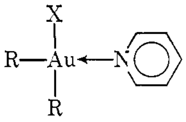
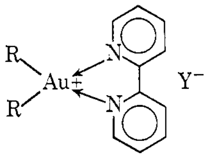
Abstract: A series of 1:1 complexes of dimethylgold halides and pseudohalides with 2,7-dimethyl-1,8-naphthyridine has been prepared and characterized by elemental analysis, molecular weight, conductivity, and spectral data. A study of the temperature dependence of the proton magnetic resonance spectra revealed a fluxional behavior of these nonionic molecular compounds in dichloromethane and chloroform solutions. Whereas at very low temperatures the gold atom is associated with only one of the two nitrogen donors of the ligand, there is rapid intramolecular two-site exchange at elevated temperatures (>200°K). It is only above ambient temperature that the intermolecular exchange of ligand and/or (pseudo)halide ion becomes rapid on the nmr time scale, whereby the low-temperature nonequivalence of the two methyl groups attached to gold is eliminated. Analogous dimethylgold halide complexes of 2,2′-bipyridyl, on the contrary, are classical ionic chelate compounds, which do not show this kind of nonrigidity.

In the course of studies in organogold chemistry[3] we have investigated complexes of dimethylgold halides and pseudohalides with 1,8-naphthyridine. It was anticipated that these novel coordination compounds should possibly show the characteristics of nonrigid molecules, similar to those found earlier in complexes of other, chemically quite different, monofunctional acceptors and 1,3-difunctional donors.[4,5]

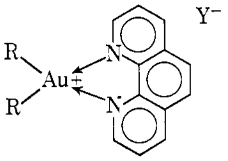
It had already been demonstrated in the pioneering work of Gibson, *et al.*, that dialkylgold derivatives form stable adducts with nitrogen donors and, in particular, with pyridine[6,7] as well as with 2,2′-bipyridyl[8–11] and phenanthroline.[11] More recent studies by Tobias, *et al.*,[12,13] and in our laboratory[14] have provided additional, primarily spectroscopic data. From this work it again appeared that whereas pyridine leads to molecular, nonionic 1:1 complexes only, which invariably possess the cis-structure A, 2,2′-bipyridyl and phenanthroline typically afford ionic, chelated species B and C, respectively.



A



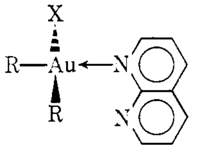
B



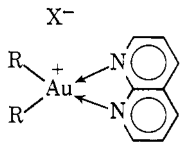
C

R = alkyl, X = halogen, Y = NO_3, AuX_2, R_2AuX_2

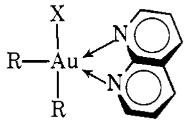
With the naphthyridine ligand then, basically, two possible structures, D and E, could be anticipated and, in addition, a pentacoordinate structure F of a type not previously known.[15] The chelate interaction in E would require a highly strained four-membered ring system, since the nitrogen lone pair electrons are in orbitals parallel to each other and would therefore interact less favorably with the gold orbitals. This strain is absent in the bipyridyl and phenanthroline systems B and C, where the nitrogen lone pairs can be favorably oriented toward the metal atoms. The close proximity of a second donor site in structure D should result in very low activation energies for an intramolecular 1,3 shift of the gold atom similar to the "oscillation" found for some complexes of aluminum, gallium, and indium[4] alkyls, as well as for analogous silicon, germanium,[5] and phosphorus[16] compounds, with 1,3-bisimino donors (eq 1).



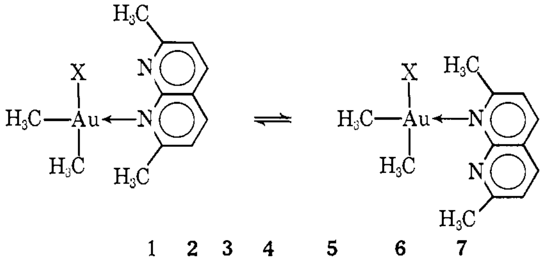
D



E



F



(1)

1 2 3 4 5 6 7

X = Cl Br I OCN SCN SeCN CN

In order to facilitate evaluation of nmr spectra the ligand 2,7-dimethyl-1,8-naphthyridine was chosen,

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[1] Organogold Chemistry, Part XIII. For parts XI and XII, see H. Schmidbaur and K. C. Dash, *Chem. Ber.*, **105**, 3662 (1972); K. C. Dash and H. Schmidbaur, *ibid.*, **106**, 1221 (1973).

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[3] For other parts see ref 1 and earlier papers quoted therein.

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[11] W. L. Gent and C. S. Gibson, *ibid.*, 1835 (1949).

[12] G. C. Stocco and R. S. Tobias, *J. Amer. Chem. Soc.*, **93**, 5057 (1971).

[13] F. Stocco, G. C. Stocco, W. M. Scovell, and R. S. Tobias, *Inorg. Chem.*, **10**, 2639 (1971).

[14] H. Schmidbaur, A. Shiotani, and K. C. Dash, unpublished work 1969–1971. Some of these results are included in this paper.

[15] B. Armer and H. Schmidbaur, *Angew. Chem.*, **82**, 120 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 101 (1970), a review article on organogold chemistry.

[16] T. Winkler, W. v. Philipsborn, J. Stroh, and E. Zbiral, *Chem. Commun.*, 1645 (1970); O. J. Scherer and R. Schmitt, *J. Organometal. Chem.*, **16**, P11 (1969); O. J. Scherer and P. Hornig, *Chem. Ber.*, **101** 2533 (1968).

where a possible nonequivalence of the two fused pyridine rings is particularly easy to detect by the nonequivalence of the two methyl resonances. The ligand properties of this compound have been studied extensively by Hendricker, *et al.*,[17–19] in recent years, but, surprisingly, in no case has a nonrigidity phenomenon been discovered.

For comparison, results on the synthesis and properties of the pyridine and 2,2′-bipyridyl complexes of dimethylgold chloride are included in the discussion and described in the Experimental Section. Compounds **1**–**7** (eq 1) containing the naphthyridine ligand have been prepared by straightforward procedures and their properties are studied in greater detail.

Experimental Section

Materials. Dimethylgold halides were prepared as described earlier,[1] thereby following established procedures, slightly modified in recent years.[12,15,21–23] Dimethylgold cyanide,[13] cyanate,[13] thiocyanate,[1,11,24] and selenocyanate[24] were similarly synthesized according to literature methods. The 2,7-dimethyl-1,8-naphthyridine, prepared *via* the route described by Paudler and Kress,[25] was kindly supplied by Dr. W. Wolfsberger of this laboratory.[26] All compounds were handled under an atmosphere of dry purified nitrogen and all solvents were dried, purified, and degassed accordingly.

Analysis and Spectra. C, H, and N analysis were carried out in this laboratory by Mrs. E. Ullrich. Molecular weights were determined by osmometry (Mechrolab 302) as well as by standard cryoscopy in a closed Beckmann system. Conductivity was measured with a commercial WTW bridge, Model LF 39. Infrared spectra were recorded on a Perkin-Elmer 457 instrument (400–250 cm^{-1}) for Nujol mulls between CsI plates. Varian instruments T 60, A 60, and XL 100, all with variable temperature probes, were used for the nmr spectra. Temperature control was by insertion of standard methanol samples. A Varian MAT SM1-BH mass spectrometer was available for preliminary mass spectrum measurements. Raman spectra were taken with a Cary 83 spectrometer. All melting points were determined in sealed capillaries and are uncorrected.

Synthetic Work. (2,7-Dimethyl-1,8-naphthyridine)–Chlorodimethylgold, DMN · $(CH_3)_2AuCl$ (1). Dimethylgold chloride (0.211 g, 0.8 mmol based on the monomeric formula) was dissolved in 7 ml of *n*-hexane and added to a solution of 0.128 g of DMN (2,7-dimethyl-1,8-naphthyridine) (0.8 mmol) in a mixture of 2 ml of *n*-hexane and 1 ml of chloroform at 0°. A white precipitate was formed almost immediately. Stirring was continued for 30 min, and the product was filtered, washed with *n*-hexane, and dried *in vacuo* (0.30 g, ~91% yield) (mp 110° dec).

Anal. Calcd for $C_{12}H_{16}AuClN_2$: C, 34.25; H, 3.83; N, 6.65; mol wt, 420.7. Found: C, 34.1; H, 3.9; N, 6.6; mol wt, 428 (cryoscopy in benzene), 424 (osmometry in chloroform).

(2,7-Dimethyl-1,8-naphthyridine)–Bromodimethylgold, DMN · $(CH_3)_2AuBr$ (2). This compound was obtained similarly in the form of white shining plates from 0.102 g of $(CH_3)_2AuBr$ and 0.052 g of DMN (0.33 mmol each) in the same solvents (0.132 g, ~86% yield) (mp 125° dec).

Anal. Calcd for $C_{12}H_{16}AuBrN_2$: C, 30.98; H, 3.47; N, 6.02; mol wt, 465.2. Found: C, 31.0; H, 3.8; N, 5.9; mol wt, 461 (cryoscopy in benzene).

(2,7-Dimethyl-1,8-naphthyridine)–Iododimethylgold, DMN · $(CH_3)_2AuI$ (3). Again 0.101 g of $(CH_3)_2AuI$ and 0.045 g of DMN (0.28 mmol) gave 0.126 g of product (87% yield) from *n*-hexane–chloroform 14:1 (v/v) as a colorless precipitate.

Anal. Calcd for $C_{12}H_{16}AuN_2I$: C, 28.13; H, 3.15; N, 5.47; mol wt, 512.2. Found: C, 28.2; H, 3.45; N, 5.30; mol wt, 529 (cryoscopy in benzene).

(2,7-Dimethyl-1,8-naphthyridine)–Isocyanatodimethylgold, (DMN) · $(CH_3)_2AuOCN$ (4). $(CH_3)_2AuOCN$ (0.183 g) and 0.106 g of DMN (0.68 mmol each) yielded 0.23 g of product, white shining plates (79.5%) (mp 95° dec) from the same *n*-hexane–chloroform mixture.

Anal. Calcd for $C_{13}H_{16}AuN_3O$: C, 36.54; H, 3.77; N, 9.83; mol wt, 427.3. Found: C, 36.8; H, 3.91; N, 9.50; mol wt, 437 (cryoscopy in benzene).

(2,7-Dimethyl-1,8-naphthyridine)–Thiocyanatodimethylgold, (DMN) · $(CH_3)_2AuSCN$ (5). From 0.13 g of $(CH_3)_2AuSCN$ and 0.072 g of DMN (0.45 mmol each) in the same solvent, 0.14 g of product (70% yield) was obtained (mp 100°).

Anal. Calcd for $C_{13}H_{16}AuN_3S$: C, 35.21; H, 3.64; N, 9.48; mol wt, 443.4. Found: C, 35.2; H, 3.80; N, 9.44; mol wt, 447 (osmometry in $CHCl_3$).

(2,7-Dimethyl-1,8-naphthyridine)–Selenocyanatodimethylgold, (DMN) · $(CH_3)_2AuSeCN$ (6). $(CH_3)_2AuSeCN$ (0.178 g) and 0.084 g of DMN (0.53 mmol each) yielded 0.185 g of crystalline product (71%) from 22 ml of *n*-hexane and 1 ml of chloroform at 0° (mp 99° dec).

Anal. Calcd for $C_{13}H_{16}AuN_3Se$: C, 31.85; H, 3.29; N, 8.57; mol wt, 490.25. Found: C, 31.7; H, 3.51; N, 8.24; mol wt, 484 (cryoscopy in benzene).

(2,7-Dimethyl-1,8-naphthyridine)–Cyanodimethylgold, (DMN) · $(CH_3)_2AuCN$ (7). In order to avoid much handling of the explosive, shock-sensitive $(CH_3)_2AuCN$, the procedure was changed as follows. $(CH_3)_2AuCl$ (0.277 g, 1.06 mmol) was dissoved in 8 ml of petroleum ether (30–60°) and stirred with a solution of 0.182 g of $AgNO_3$ (1.07 mmol) in 20 ml of water. After filtration, evaporation of the solvent, and cooling of the aqueous phase to 0°, 0.071 g of KCN dissolved in 3 ml of water was added, and the precipitate was filtered, washed with water and methanol, and dried *in vacuo*. The crude $[(CH_3)_2AuCN]_4$ thus obtained was immediately redissolved in 20 ml of *n*-pentane, and the solution was filtered directly into a solution of 0.084 g of DMN (0.53 mmol, assuming a 50% yield of dimethylgold cyanide) in a mixture of 13 ml of *n*-hexane and 1 ml of chloroform at 0°. The fine white precipitate, after stirring for 30 min, was collected on a frit, washed with *n*-hexane thoroughly to remove any excess unreacted dimethylgold cyanide, and dried *in vacuo* (yield 0.13 g) (mp 120° dec).

Anal. Calcd for $C_{13}H_{16}AuN_3$: C, 37.96; H, 3.92; N, 10.22; mol wt, 411.3. Found: C, 37.6; H, 4.23; N, 9.94; mol wt, 412 (cryoscopy in benzene).

2,2′-Bipyridyldimethylauric Dichlorodimethylaurate, $[(bipyr)Au(CH_3)_2]^+[Cl_2Au(CH_3)_2]^-$ (8). $(CH_3)_2AuCl$ (0.20 g, 0.76 mmol) was dissolved in 6 ml of *n*-hexane and added with stirring to a solution of 2,2′-bipyridyl (bipyr, 0.119 g, 0.76 mmol) in 10 ml of the same solvent containing 1 ml of chloroform. After filtration of the precipitate, washing with *n*-hexane, and drying *in vacuo*, a yield of 0.232 g (88.5%) was obtained (mp 118° dec).

Anal. Calcd for $C_{14}H_{10}Au_2Cl_2N_2$: C, 24.68; H, 2.96; N, 4.11. Found: C, 25.0; H, 3.1; N, 4.1.

The known analogous $[(bipyr)Au(C_2H_5)_2]^+[Br_2Au(C_2H_5)_2]^-$ was prepared under slightly different experimental conditions.[10] The procedure used here is identical with that used to synthesize the DMN complexes!

2,2′-Bipyridyldimethylauric Dichloroaurite, $[(bipyr)Au(CH_3)_2]^+[AuCl_2]^-$. **8** (0.13 g) was warmed on a water bath in 20 ml of ethanol. The compound slowly dissolved completely and after a short interval, a gas evolution accompanied by a precipitation of colorless needles occurred. Yield after filtration, washing with ethanol, and drying *in vacuo* was 0.11 g (88%) (mp 165° dec).

Anal. Calcd for $C_{12}H_{14}Au_2Cl_2N_2$: C, 22.13; H, 2.17; N, 4.55. Found: C, 22.3; H, 2.30; N, 4.26.

Chlorodimethyl(pyridine)gold, $(CH_3)_2AuCl(pyr)$ (10). This compound was first prepared by Tobias, *et al.*[12] We obtained a product with the same properties as described by these authors, but used the

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(25) W. W. Paudler and T. J. Kress, *J. Heterocycl. Chem.*, 4, 284 (1967).

(26) We are indebted to Dr. Hendricker for helpful information concerning more recent pertinent literature, 1969.

procedure applied for the synthesis of the DMN complexes under report. Under these conditions no compound other than the 1:1 adduct could be obtained, even when a large excess of the ligand was used.

Attempts to prepare complexes of DMN with dimethylgold nitrate and perchlorate were unsuccessful.

Results

Naphthyridine Complexes. 2,7-Dimethyl-1,8-naphthyridine (DMN) has been found to form only 1:1 complexes with dimethylgold chloride, bromide, iodide, cyanate, thiocyanate, selenocyanate, and cyanide (**1**–**7**). The same product was obtained regardless of whether excess halide or pseudohalide or excess DMN was used in the syntheses. Well defined 1:1 complexes were isolated in all cases and the excess reactant was recovered from the filtrate. All compounds are colorless crystalline solids, soluble in dichloro- and trichloromethane, benzene, toluene, and acetone. The solubility in aliphatic hydrocarbons and in ether is very low.

Cryoscopic and/or vapor pressure osmometric molecular weight determinations in benzene and, in some cases, in chloroform showed the compounds to exist as monomers in these solvents. The values obtained were very close to the formula weights.

Measurements of electric conductivity in acetone solutions provided values corresponding to nonelectrolytes at ambient temperatures and concentrations of *ca.* 1×10^{-3} *M*. Typical data are presented in Table I.

Table I. Conductivity Values of Organogold(III) Compounds in Acetone

Compd no.	Molar concn (10^{-3} *M*)	Temp, °C	Λ_M,[a] cm^2 ohm^{-1} mol^{-1}
1	0.71	22	0.35
2	0.90	21	3.8
3	1.09	21.5	1.8
4	1.26	20.5	1.3
5	1.08	21	3.6
6	1.32	21.5	3.5
7	1.73	24	13.6
8	1.5	21	113.5
9	1.2	21	118.4

[a] A 2.1×10^{-3} *M* solution of $AgBF_4$ in acetone gave a conductivity of 112 cm^2 ohm^{-1} mol^{-1} at 21°.

The DMN complexes are not volatile without decomposition and mass spectrometry indicated only the presence of fragments in the vapor phase. At an ionization energy of 70 eV and inlet temperatures up to 50° the ions of the ligand and the mass spectrum pattern known to be typical for dimethylgold halides and pseudohalides[1] were observed.

The infrared spectra are quite complicated due to the many absorptions of the DMN ligands. It is possible, however, to assign many of the bands on the basis of earlier work on naphthyridine complexes,[13–20] and other dimethylgold derivatives.[12,13,21–24] The pseudohalides **4**–**7** show strong absorptions for the OCN, SCN, SeCN, and CN moieties, some of which have been tabulated in Table II together with a series of characteristic bands of the $(CH_3)_2Au$ moieties. From the observed values of $\nu(C{\equiv}N)$ it may be concluded that the pseudohalide groups are not attached to the metal through the nitrogen, but rather through the other end of the groups (O, S, Se, C). In the selenium case there is supporting evidence from nmr spectroscopy (*vide infra*). Gold–halogen stretching frequencies were difficult to identify in the infrared as several but only weak bands were found in the critical region of 250–350 cm^{-1}.

Table II. Important Absorptions in the Vibrational Spectra of the Dimethylnaphthyridine Complexes (cm^{-1})

	δ_{CH_3Au}		ν_{AuC}		$\nu_{C{\equiv}N}$
No.	Ir	R	Ir	R	Ir
1	1235 m		572 m		
	1222 m		511 w		
	1205 vs				
2	1231 s		575 sh		
	1222 s		568 s		
	1200 vs		511 m		
3	1228 s		571 w		
	1219 m		549 s		
	1204 w		535 s		
	1192 s				
4	1245 w		575 m		2206 vs[b]
	1218 sh		572 m		2176 w
	1212 s		501 m		
5[a]	1238 s	1234 w	563 m	563 s	2122 vs[c]
	(1222 m)			552 s	
	1198 vs	1196 w	503 m		
6	1231 s		578 m		2121
	1218 s		539 s		
	1205 m		515 m		
	1191 s		509 s		
7	1236 s	1237 w	568 m	568 s	2143 vs[d]
	1222 s			560 s	
	1209 s		510 s		
	1204 sh	1204 w			

[a] 245 (R) ν_{AuS}. [b] 2210 for $(CH_3)_2AuOCN \cdot P(C_6H_5)_3$.[13] [c] 2120 for $(CH_3)_2AuSCN \cdot P(C_6H_5)_3$.[13] [d] 2156 for $(CH_3)_2AuCN \cdot P(C_6H_5)_3$.[13]

Raman spectra could be obtained only for the thiocyanate **5** and the cyanide **7**. All other DMN complexes decomposed too rapidly when exposed to the laser beam. The most intense bands were found in the 500–600-cm^{-1} region, where the Au–C stretching vibrations are active.[12] Most of the frequencies. coincide with the weaker ir absorptions (Table II). The same is true for the weak Raman bands in the CH_3(Au) deformation range (1180–1250 cm^{-1}). A weak Raman line at 245 cm^{-1} for **5** can be tentatively assigned to the Au–S stretching mode. The shifts observed in the various ligand absorptions in the infrared have not been followed, as no direct information as to the structure of the molecules was to be expected.

Nmr Spectra. At room temperature for all of the seven naphthyridine complexes proton magnetic resonance spectra were obtained, which showed two equivalent ligand methyl groups (DMN), but two nonequivalent methyl groups attached to gold. A single AB pattern of the two equivalent sets of aromatic protons was also observed. Though the relative chemical shifts of these signals changed somewhat with the solvent employed—benzene, toluene, dichloromethane, and chloroform—the number and relative intensities of the peaks were unaltered under these conditions (Table III, Figure 1b).

This result was compatible with a pentacoordinate, dihapto structure F, but also with the monohapto formula D, if a process according to eq 1 was rapid on the nmr time scale, at room temperature. The complexes clearly contain the two gold methyl groups

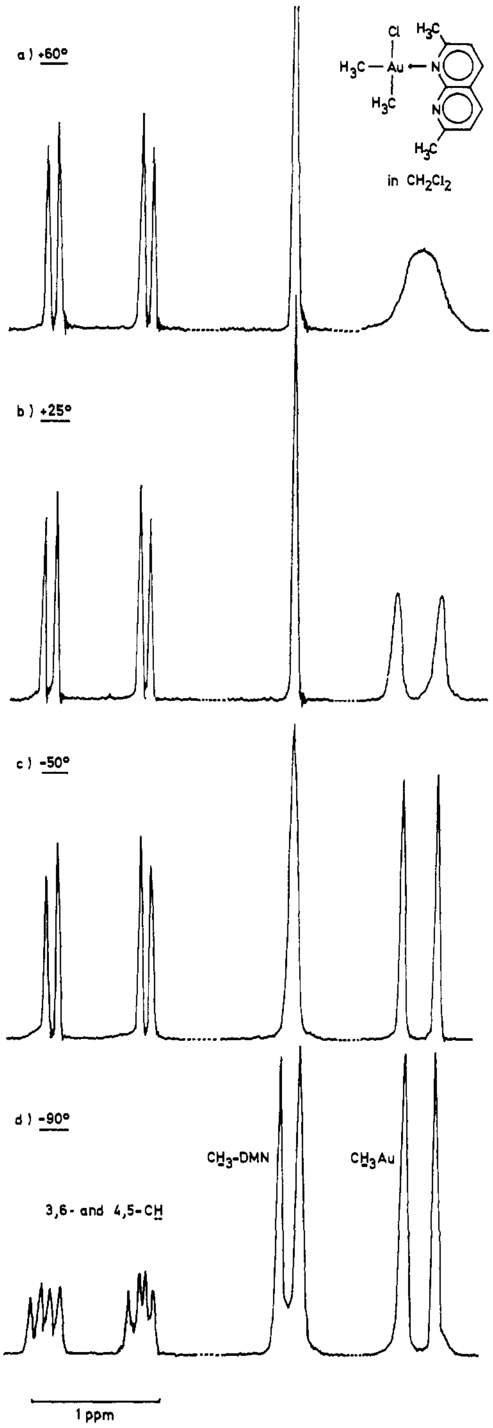


Figure 1. Proton magnetic resonance spectrum of $(CH_3)_2AuCl\cdot$DMN in dichloromethane solution at four different temperatures: a, +60°; b, +25°; c, −50°; d, −90°. Different amplitude settings were used where necessary in a 100.1-MHz spectrometer.

in a cis position, in full agreement with earlier work on other square planar, tetracoordinate dimethylgold(III) coordination compounds.[1,12,13,21,24]

At *elevated temperatures* (~60°) this nonequivalence of *cis*- and *trans*-CH_3Au is no longer preserved for most of the complexes, as these signals broaden and, in some cases, coalesce. This is not an uncommon phenomenon in organogold chemistry, as many other species are known to show the same temperature dependence of their nmr spectra. This is due to rapid ligand exchange, which finally renders the CH_3Au groups equivalent. Both X and L of an $(CH_3)_2AuXL$ compound may be involved in this process (Figure 1a).[1,12,21,24]

Table III. ^{1}H Nmr Spectra of the Dimethylgold Halide and Pseudohalide Complexes **1–8** and **10** (TMS External Standard, ppm)[a]

	δ_{CH_3Au} cis/ trans[e]	δ_{CH_3C}	$\delta_{3,6\text{-}CH}$[f]	$\delta_{4,5\text{-}CH}$[f]
1 $(CH_3)_2AuCl\cdot DMN$[b]	−1.04 −1.46	−3.05	−7.49	−8.25
2 $(CH_3)_2AuBr\cdot DMN$[b]	−1.14 −1.54	−2.99	−7.45	−8.19
3 $(CH_3)_2AuI\cdot DMN$[b]	−1.28 −1.62	−3.00	−7.48	−8.22
c	−1.25 −1.53	−3.02	−7.63	−8.39
4 $(CH_3)_2AuOCN\cdot DMN$[b]	−0.82 −1.35	−2.93	−7.47	−8.20
c	−0.77 −1.37	−3.08	−7.68	−8.44
5 $(CH_3)_2AuSCN\cdot DMN$[b]	−1.19 −1.33	−3.07	−7.61	−8.31
6 $(CH_3)_2AuSeCN\cdot DMN$[b]	−1.17 −1.24[g]	−3.03	−7.63	−8.33
d	−0.55 −0.70[g]	−1.75	−6.09	−6.80
7 $(CH_3)_2AuCN\cdot DMN$[b]	−0.50 −1.46	−2.96	−7.45	−8.30
8 $(CH_3)_2Au\cdot bipyr^+$ $(CH_3)_2AuCl_2^-$ [b]	−1.25 −1.66		Mult	~−7.5
10 $(CH_3)_2AuCl\cdot pyr$[b]	−1.20 (ref 12) −1.34 (ref 12)		Mult	

[a] **9** is too sparingly soluble in suitable solvents. [b] In $CDCl_3$. [c] In CH_2Cl_2. [d] In C_6D_6, at 32°. [e] Assignment not specified, with the exception of **6**. [f] J_{AB} = 8 Hz. [g] Selenium satellites; $J(HCAu\text{-}^{77}Se)$ = 4.7 Hz.

At room temperature the intermolecular exchange of naphthyridine in our case is still slow, however, as, for compounds **4** and **6**, with excess DMN, *two separate* sets of signals were observed, one for the free and the other for complexed DMN molecules. Upon heating, these signals broadened for **6**, but coalescence was not reached before decomposition of the sample became noticeable (*ca.* +70°). At this temperature the CH_3Au signals had already coalesced. This experiment suggests that the exchange of X is chiefly responsible for the coalescence of *cis*- and *trans*-CH_3Au signals.

With the cyanate **4** both CH_3Au and DMN–CH_3 signals remained sharp at +70°, in C_6D_6. For this compound exchange of the OCN *and* naphthyridine ligands is still slow even at reflux temperature of the benzene solvent. At higher temperatures, again, decomposition occurs.

Earlier work on phosphine complexes of trimethylgold had given similar results; exchange of phosphine ligands was slow on the nmr time scale even in the presence of a large excess of ligand and at elevated temperatures.[21b]

Conclusive evidence for halide or pseudohalide exchange was obtained by examining the spectra of the selenocyanate **6** more closely. It could be demonstrated that at lower and ambient temperatures (≦20°) only one of the two CH_3Au resonances exhibits a pair of $^1HCAu^{77}Se$ satellites! These satellites have also been observed earlier[1] for $(CH_3)_2AuCl\cdot Se(CH_3)_2$ and were assigned to the *trans*-CH_3Au protons on the basis of pertinent results in the chemistry of phosphine com-

Table IV. Coalescence Temperatures, Shift Differences, and Activation Energies for Intra- and Intermolecular Exchange Processes (from Variable Temperature ^{1}H Nmr)

		Intramolecular DMN Site Exchange			Intermolecular (Pseudo)halide Exchange		
No.	Formula	T_c, °C	$\Delta\nu$,[b] Hz	$\Delta G^{\ddagger}$, kcal/mol	T_c, °C	$\Delta\nu$,[c] Hz	$\Delta G^{\ddagger}$, kcal/mol
1	$(CH_3)_2AuCl\cdot DMN$	−63	17	10.61	+70	42	17.06
2	$(CH_3)_2AuBr\cdot DMN$	−65	15	10.56	+60	36	16.64
3	$(CH_3)_2AuI\cdot DMN$	−70	15	10.30	Dec	33	
4	$(CH_3)_2AuOCN\cdot DMN$	−73	16	10.11	+76	54	16.90
5	$(CH_3)_2AuSCN\cdot DMN$	−72	15	10.19	+65	16	17.44
6	$(CH_3)_2AuSeCN\cdot DMN$	−66	14	10.54	+50	25	16.35
6[a]		−66	15	10.51			
7	$(CH_3)_2AuCN\cdot DMN$	. . .[d]	. . .[d]		Dec	96	

[a] In the presence of excess DMN. [b] At 100.1 MHz, −90°, in CH_2Cl_2. [c] At 100.1 MHz, +10°, in $CHCl_3$. [d] Not measured because of dissociation (see text).

plexes.[21a] On heating the solution of **6** the satellites disappear at *ca.* 35°. The phenomenon is reversible.

Below ca. −60°, with solutions of each of the compounds **1**–**7** in dichloromethane, the signals of the naphthyridine ligand broaden and split into pairs. At −90° two singlets of equal intensity are registered for the DMN methyl groups along with two AB quartets, also of equal intensity, for the aromatic protons in the 3,4 and 5,6 positions, respectively (Figure 1d).

As mentioned above, addition of excess DMN ligand to the samples leads to *separate* signals for the DMN molecules, also at low temperature. Free ligand is thus *not* involved in the exchange process in this system. The coalescence temperatures, moreover, were not shifted by changes in the concentrations of the complexes within the standard deviations of the experiment (*ca.* ±5°).

The individual coalescence temperatures depend slightly on the nature of the halide or pseudohalide substituent, and are lowest for X = OCN and highest for X = Cl. From these values and differences in chemical shifts of the nonequivalent DMN–CH_3 resonances at −90° (Table IV), the activation energies for the process according to eq 1 have been calculated.[27] Similarly $\Delta G^{\ddagger}$ values have been estimated from the coalescence of the $(CH_3)_2Au$ signals. These results are also included in Table IV.

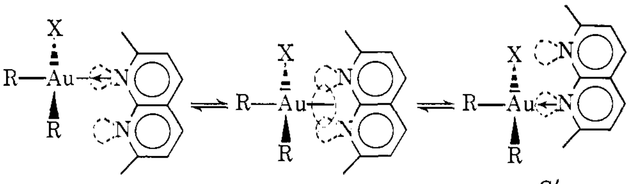
Some special features of the spectra of the cyanide **7** must be mentioned here. This compound, which gave correct analytical results (see Experimental Section), appeared to dissociate in solution above +10° into free DMN ligand and some dimethylgold cyanide tetramer.[13] Signals for these dissociation products were observed in addition to those of the complex itself, which at elevated temperature again coalesced in a fully reversible manner, as a consequence of rapid exchange. Dissociation phenomena of this type have been described earlier in the literature, *e.g.*, for $(CH_3)_2AuSCN\cdot pyr$.[12] The dissociation of **7** was not yet noticeable in the molecular weight determinations conducted in freezing benzene.

Pyridine and Bipyridyl Complexes. Dimethylgold chloride was found to form 1:1 complexes only with pyridine, but 2:1 complexes with 2,2′-bipyridyl, as shown in[12] or expected from[10] earlier results. Whereas the former (**10**) is a nonionic compound, possessing the cis structure A and undergoes rapid ligand exchange in solution, the complex $[(CH_3)_2AuCl]_2\cdot bipyr$ (**8**) clearly appears to be an ionic solid, highly conducting in solution (Table I). Its nmr spectrum (in chloroform) shows two sharp $(CH_3)_2Au$ resonances, which in this case can be assigned to the methyl groups of the cations and of the anions, respectively, according to formula B (Table III). Thermal decomposition in boiling ethanol turns **8** into **9**, the $(CH_3)_2AuCl_2^-$ anion being converted into the $AuCl_2^-$ counterion through loss of ethane. For this product only one CH_3Au signal remains in pmr. The conductivity, however, is largely unchanged (Table I).

Discussion

The control experiments with pyridine and 2,2′-bipyridyl under standard conditions have confirmed that dimethylgold halides are able to form complexes with these mono- and bidentate ligands both of the monohapto and of the dihapto form, A and B, respectively. The failure of 2,7-dimethyl-1,8-naphthyridine to act as a bidentate donor with the same organometallic components must have its origin in the special parallel orientation of the nitrogen lone pairs of electrons of the two rigidly fused pyridine rings.[28] Orbital overlap not only would be poor for the chelate E containing a four-membered ring system, because the nitrogen lone pairs cannot be properly directed to the metal (as it is possible in the bipyridyl analogs), but also for a pentacoordinate structure F.

For gold(III), in a square-planar valence state, interaction with a single ligand orbital is favored, as drawn in G and G′, rather than bonding to two closely spaced orbitals of the difunctional donor as in H.



G H G′

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[27] A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Phys. Chem.*, 67, 280 (1963).

[28] From crystallographic studies by Bernal, *et al.*, on tetrakis(1,8-naphthyridine)iron(II) perchlorate, the geometry of the ligand is precisely known and the "bite" of the chelating agent found to be only ~2.1 Å. Moreover, this complex is notable in that it contains one out of the four naphthyridines in what could be referred to as a monohapto interaction. The two Fe–N distances in this case differ by ~0.5 Å (2.178 and 2.756 Å), while in all other cases an almost symmetrical bonding of the ligand (dihapto!) is observed (2.2–2.46 Å for Fe–N): A. Clearfield, P. Singh, and I. Bernal, *Chem. Commun.*, 389 (1970).[29]

[29] NOTE ADDED IN PROOF: D. Gatteschi, C. Mealli and L. Sacconi (*J. Amer. Chem. Soc.*, **95**, 2736 (1973)) have reported the crystal structure of a binuclear naphthyridine complex of lower valent nickel.

Though this symmetrical interaction is higher in energy, it seems to be a very favorable transition state or intermediate for the observed intramolecular rearrangement according to eq 1, *i.e.*, $G \rightleftharpoons G'$. At least it is superior to that of a largely intermolecular dissociation–recombination mechanism, as shown by the differences in activation energies for both processes (Table IV).

The presence of two methyl groups in the 2 and 7 positions of the ligands are likely to preclude a coplanar arrangement of the planar dimethylgold (pseudo)halide unit and the ligand. The relative orientation of the two parts of the complexes during the intramolecular rearrangement process is not known, however. It is possible that a perpendicular orientation is preferred. A determination of the crystal structure of one of the compounds should provide at least indirect information on that point.

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Orbital Noninteraction in Bridged Cyclohexanes

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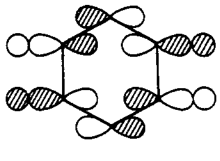
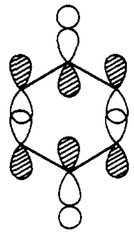
Abstract: The highest occupied σ orbitals in six-membered rings possess interesting symmetry properties. In the bicyclo[2.2.1]heptane skeleton the consequent inability of these levels to interact with any orbitals of the one-carbon bridge results in an unusual destabilization of the 7-norbornyl cation and a stabilization of the oxygen p-type lone pair of 7-oxanorbornane.

Diverse are the spectroscopic and chemical consequences of orbital interaction through space and through bonds.[2] In this contribution we discuss a curious case of structurally enforced absence of orbital interaction, with significant chemical implications.

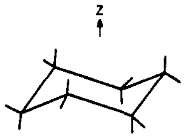
In benzene there is found a high-lying degenerate set of σ orbitals, e_{2g} in D_{6h} symmetry. In the notation of Lindholm,[3] these are a mixture of radial and tangential C 2p orbitals. In the photoelectron spectrum of benzene, the 11.4 eV ionization potential is assigned to this e_{2g} orbital set.[3] The e_{2g} orbitals can be represented in various ways but are most easily spotted and remembered as a set of horizontal and vertical waves (**1** and **2**). We have come to term them "ribbon orbitals."[4]



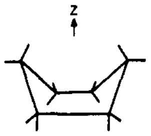
AA
1



SS
2



3



4

The ribbon orbitals are not peculiar to benzene but recur in any system with a six carbon cycle. They are the highest lying molecular orbitals, e_g in D_{3d} symmetry, in a chair cyclohexane structure (**3**). In the boat cyclohexane structure (**4**), the lowered C_{2v} symmetry finally forces a splitting of the formerly degenerate levels. SS (**2**, a_1 in C_{2v}) comes below AA (a_2, **1**) by 0.26 eV in an extended Hückel[5a] or 0.34 eV in a CNDO/2[5b] calculation. The primary determinant of the observed level ordering appears to be the antibonding H–H interaction among the side equatorial hydrogens in AA. Both AA and SS ribbon orbitals acquire some *z* component in the chair and boat cyclohexane structures, but their in-plane nature, as represented by the structures **1** and **2**, remains dominant. Indeed, the ribbon orbitals persist in any molecule which incorporates a six-membered ring, and representations of them may be found in the literature for molecules as diverse as **5**, triasterane,[6] the

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(1) Part 49 of "Applications of Photoelectron Spectroscopy." Part 48: M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, in press.

(2) (a) See previous papers in the series "Applications of Photoelectron Spectroscopy." (b) R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971); R. Hoffmann and W.-D. Stohrer, "Special Lectures at XXIIIrd International Congress of Pure and Applied Chemistry," Vol. 1, Butterworths, London, 1971, p 157.

(3) B.-Ö. Jonsson and E. Lindholm, *Ark. Fys.*, **39**, 65 (1969); *Chem. Phys. Lett.*, **1**, 501 (1967).

(4) Still better representations of these orbitals may be found in W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals," Academic Press, New York, N. Y., 1973.

(5) (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962). A hydrogen exponent of 1.3 was used. (b) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, S 136 (1965) and subsequent papers.

(6) E. Haselbach, E. Heilbronner, H. Musso, and A. Schmelzer, *Helv. Chim. Acta*, **55**, 302 (1972).